

## PATENT SPECIFICATION

NO DRAWINGS

L170.663

L170.663



Inventor: FREDDY WATTIMENA and GERRIT DE KRIJGER

Date of Application (No. 13486/67): 22 March, 1967.

Patents Act 1949): 15 Feb., 1968.

Date of Application (No. 13486/67): 22 March, 1967.

Date of Application (No. 49261/67): 30 Oct., 1967.

Complete Specification Published: 12 Nov., 1969.

Index at acceptance:—B1 E(20Y, 202, 21Y, 215, 23X, 238, 239, 25Y, 253, 271, 275, 277, 32Y, 320, 33Y, 331, 55Y, 551, 562, 574, 644, 662, 663, 691, 692, 693); C2 C(B4B, B4H)

International Classification:—B 01 j 11/20

## COMPLETE SPECIFICATION

## Process for preparing Silver Catalysts

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bvlandtlaan, The Hague, The

liquid adsorbed by the porous solid substance is evaporated in at most 900 seconds and reduction occurs simultaneously.

Hereinafter, the treatment to effect simul-

## ERRATUM

SPECIFICATION No. 1,170,663

Page 1, Heading, *delete* "Date of Application (No. 13486/67): 22 March, 1967." (first occurrence), *insert* "Date of filing Complete Specification (under Section 3 (3) of the"

THE PATENT OFFICE  
22nd December 1969

the reaction to be catalyzed. The catalytically active material comprises silver and occasionally an oxide thereof. Such a material is usually most conveniently applied to the surface of the particles by wetting or impregnating the carrier material with a solution of one or more salts of silver and after that evaporating the solvent. The substance or substances dissolved in the liquid used in the impregnation stage do not as such form the desired catalytically active material, which has then to result from a chemical conversion viz. a reduction. It is as a rule advantageous to effect that this reduction will take place during the evaporation of the solvent.

The present invention provides a process for the preparation of a silver containing catalyst which comprises impregnating a particulate solid porous substance with a solution of a reducible silver compound and subsequent evaporation of the solvent by intimately contacting the particulate porous solid substance with a heated gaseous atmosphere under such conditions that at least 80% by volume of the

room temperature or with moderate heating may precede the shock-drying.

The shock-drying is effected by means of a heated gas stream. It is often convenient when using this method to pass the material to be shock-dried countercurrently through the stream of gas, e.g. by letting the particles fall down in a stream of gas which is directed upwards. It will be appreciated that the most suitable conditions, including temperatures and, within the limits set above, also heating times are dependent on the volatility of the liquid. Reduced pressures may be applied to increase the evaporation, if necessary or desired.

Of course, the conditions of the shock-drying have to be adapted not only to the volatility of the solvent but also on the rate of the reduction which has to take place so that it will proceed to a sufficient extent.

If between impregnation and shock-drying treatment part of the solvent is removed by pre-drying at room temperature or with moderate heating, this should not in any way

SEE ERRATA SLIP ATTACHED

BEST AVAILABLE COPY

## PATENT SPECIFICATION

NO DRAWINGS

L170.663

L170.663



Inventor: FREDDY WATTIMENA and GERRIT DE KRIJGER

Date of Application (No. 13486/67): 22 March, 1967.  
Patents Act 1949): 15 Feb., 1968.

Date of Application (No. 13486/67): 22 March, 1967.

Date of Application (No. 49261/67): 30 Oct., 1967.

Complete Specification Published: 12 Nov., 1969.

Index at acceptance:—B1 E(20Y, 202, 21Y, 215, 23X, 238, 239, 25Y, 253, 271, 275, 277, 32Y, 320, 33Y, 331, 55Y, 551, 562, 574, 644, 662, 663, 691, 692, 693); C2 C(B4B, B4H)

International Classification:—B 01 j 11/20

## COMPLETE SPECIFICATION

## Process for preparing Silver Catalysts

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of a silver containing catalyst which consists of a particulate solid porous substance (also to be called the carrier material) with a catalytically active silver comprising substance or composition present as a thin layer on the surface of the particles, including the inner surface of the pores. The particles as such, have, of course, to consist of some material which does not adversely affect the reaction to be catalyzed. The catalytically active material comprises silver and occasionally an oxide thereof. Such a material is usually most conveniently applied to the surface of the particles by wetting or impregnating the carrier material with a solution of one or more salts of silver and after that evaporating the solvent. The substance or substances dissolved in the liquid used in the impregnation stage do not as such form the desired catalytically active material, which has then to result from a chemical conversion viz. a reduction. It is as a rule advantageous to effect that this reduction will take place during the evaporation of the solvent.

The present invention provides a process for the preparation of a silver containing catalyst which comprises impregnating a particulate solid porous substance with a solution of a reducible silver compound and subsequent evaporation of the solvent by intimately contacting the particulate porous solid substance with a heated gaseous atmosphere under such conditions that at least 80% by volume of the

liquid adsorbed by the porous solid substance is evaporated in at most 900 seconds and reduction occurs simultaneously.

Hereinafter, the treatment to effect simultaneous evaporation and reduction will be referred to as "shock-drying" treatment.

Preferably, at least 90% by volume of the liquid is evaporated in at most 300 seconds. Most preferably, substantially complete evaporation is effected in a time between 0.5 and 120 seconds. In those cases where the liquid to be removed mainly or entirely consists of water, preferred evaporation times are as a rule in the range of from 2 to 30 seconds.

Prior to the shock-drying treatment part of the liquid originally present may be removed, if necessary or desired, by such methods as, for instance, decantation, centrifugation or filtration. Moreover, pre-drying by evaporation at room temperature or with moderate heating may precede the shock-drying.

The shock-drying is effected by means of a heated gas stream. It is often convenient when using this method to pass the material to be shock-dried countercurrently through the stream of gas, e.g. by letting the particles fall down in a stream of gas which is directed upwardly. It will be appreciated that the most suitable conditions, including temperatures and, within the limits set above, also heating times are dependent on the volatility of the liquid. Reduced pressures may be applied to increase the evaporation, if necessary or desired.

Of course, the conditions of the shock-drying have to be adapted not only to the volatility of the solvent but also on the rate of the reduction which has to take place so that it will proceed to a sufficient extent.

If between impregnation and shock-drying treatment part of the solvent is removed by pre-drying at room temperature or with moderate heating, this should not in any way

SEE ERRATA SLIP ATTACHED

adversely affect the chemical reduction. Losses of substances involved in this conversion have to be avoided, and, in general, care should be taken to ensure that the amount of the catalytically active material be not unduly reduced by any treatment preceding the shock-drying. This is of particular importance when applying a pre-treatment consisting of or including a method as, for instance, decantation, centrifugation or filtration.

There is a particularly advantageous embodiment of the process of invention which is applicable for drying particulate solid materials consisting of porous particles in which the maximum distance along a straight line between two points of the space taken up by any one particle is in the range of from 1 to 25 mm, in particular of from 2 to 9 mm, and especially in the range of from 3 to 7 mm. For this maximum distance the term "maximum particle diameter" will henceforward be employed. Of course, if a particle is spherical in shape, the maximum particle diameter is identical with the diameter of the sphere. However, in general, the particles will have rather irregular shapes. It is possible to impregnate and shock-dry particles larger than are eventually to be used and to break these up following the shock-drying treatment so as to obtain catalyst particles of such a size as is preferable for the catalyst to be used in the chemical process concerned.

Particles having a maximum diameter in the range of from 1 to 25 mm, in particular of from 2 to 9 mm, and especially in the range of from 3 to 7 mm, are advantageously shock-dried by allowing them to fall through a heated and fluidized bed of a particulate solid substance having a much smaller maximum particle diameter, namely of at most 0.5 mm, and preferably in the range of from 0.035 to 0.35 mm. By the presence of the particles which form the fluidized bed the heat exchange between the particles to be dried and the upwardly flowing gas is considerably improved. Accordingly, the rate of flow of the drying gas may be considerably reduced, and thus the total amount of the said gas which is required per kilogram of the particulate solid material to be dried is much less than would otherwise have been the case.

The inert particles forming the fluidized bed and having a maximum particle diameter of at most 0.5 mm may be porous. However, in that case they should preferably, have such a pore structure as to provide a relatively small total surface area. In general, a total surface area of less than one m<sup>2</sup> per gram has been found desirable. Suitable porous materials include, for instance, pumice, ceramic materials, silicon carbide, silicon oxide, aluminas, and silica-aluminas. It is, however, preferable to employ inert particles which are free of pores. These, may, for instance, consist of such materials as glass or quartz.

The catalysts prepared, hereinafter briefly to be denoted by the term "silver catalysts", are rather widely employed in oxidation processes involving the use of molecular oxygen as the oxidizing agent, for instance, the oxidation of lower olefins, in particular ethylene, to the corresponding olefin oxides, that is to ethylene oxide when ethylene is the starting material.

Porous particulate solid substances suitable for the preparation of silver catalysts include all such conventional carrier materials as, for instance, pumice, ceramic materials, silicon carbide, silicon oxide, aluminas and silica-aluminas. Very suitable is alpha-alumina, especially when the pore volume per gram is in the range of from 0.15 to 0.30 millilitres and the surface area per gram is below 10 m<sup>2</sup>, and preferably below 1 m<sup>2</sup>. Illustrative of a carrier material which has been employed with very good results is commercially available alpha-alumina having a pore volume in the range of from 0.17 to 0.24 cc/g, a surface area in the range of from 0.050 to 0.055 m<sup>2</sup>/g.

The particles may have the form of pellets, spheres, rings, cylinders or any other form which is current in the practice of producing silver catalysts. Pellets, as commercially available, have, in general, been found to be advantageous for silver catalysts to be employed in the oxidation of ethylene to ethylene oxide.

It is a known practice to incorporate into silver catalysts one or more promoters, so as to enhance the activity and/or selectivity. Such promoters include, for instance, compounds of alkali or alkaline earth metals, lithium compounds being preferred. The compounds are, preferably, the oxides of the said metals and/or compounds which can easily be converted into the oxides, for instance by a heat treatment, if necessary in an atmosphere of oxygen or an oxygen-containing gas. Examples of such convertible compounds are the hydroxides, carbonates, nitrates, acetates, propionates, lactates and oxalates of the metals. The promoters may be added to the catalyst after the silver has been applied to the surface of the particles, but it is preferable to add them to the support material before it is impregnated with a solution of one or more silver compounds. Particularly suitable is impregnation with an aqueous solution of one or more promoters or compounds which may be converted into promoters, and subjecting the support materials to a heat treatment at a temperature between 350 and 650°C. Preferred are temperatures between 400 and 550°C, because then the best adherence of the promoters to the surface of the support particles is obtained. The heat treatment may take the form of a shock-drying treatment according to the invention but, in general, this does not present any advantages.

The proportions of the promoters in the final catalyst need not as a rule be high. Pro-

portions between 0.03 and 0.5% by weight of the metals in the promoters with respect to the weight of the support material are usually found to be very satisfactory.

5 In any case, whether or not the porous support particles have been pre-treated by incorporating therein one or more promoters, the manner in which silver catalysts may be produced whilst making use of the present invention is the same. A preferred method consists in impregnating the porous support particles with an aqueous solution of a reducible silver compound, taking care that prior to, simultaneously with, or following the impregnation also a suitable reducing agent be applied to the particles, and finally subjecting the impregnated particles to a shock-drying treatment, as hereinbefore defined, under such conditions that during the said treatment the reducible silver compound is converted into metallic silver and/or silver oxide either by the action of the reducing agent alone or by the combined effect of thermal decomposition and the action of the reducing agent.

25 The reducible silver compound may be any compound from which metallic silver may be readily obtained during the shock-drying treatment. Such compounds include, for example, silver nitrate, silver carbonate, ammoniacal silver complexes and silver salts of carboxylic acids, such as formic, acetic, propionic, malic, lactic, tartaric, salicylic, and maleic acid. It is, of course, necessary in connection with the impregnation step to select a solvent in which the silver compound, concerned is sufficiently soluble. It should, preferably, be possible to obtain concentrations of at least 10 g per litre, and, most preferably, concentrations of at least 50 g per litre. When using water as the solvent, silver nitrate may suitably be employed as the reducible silver compound. In general, the impregnation should be carried out in such a manner as to provide for a silver content of the catalyst, as finally obtained, in the range of from 3 to 25, preferably from 5 to 15% by weight with respect to the weight of the porous particulate support material.

50 Suitable reducing agents are, for example, hydrazine and hydroxylamine, but organic reducing agents are generally preferred. These include, for instance, ethanolamine, methanol, isopropyl alcohol, acetone, formaldehyde, acetaldehyde and formic acid. The most preferred organic agents are polyhydric alcohols, such as propylene glycol, butylene glycol, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, glycerol, and sugars such as glucose and sucrose. The presence of the reducing agents during the shock-drying treatment is as a rule most advantageously ensured by adding them to the solutions of silver compounds used to impregnate the support materials. In particular, when employing aqueous solutions of re-

ducible silver compounds and of polyhydric alcohols as the reducing agents, the incorporation of the polyhydric alcohols in the said aqueous solutions may be very beneficial, since these compounds are surfactants, and accordingly, facilitate the penetration of the solutions into even the smallest pores of the support particles. A very suitable polyhydric alcohol is ethylene glycol. The proportions of reducing agents and water in the solutions of silver compounds may be varied within wide limits, provided the amounts of reducing agents are balanced with the amounts of silver compounds in the solutions in order to ensure appropriate deposition of silver during the drying treatment. Ratios by weight of water to reducing agents in the range of from 20:80 to 80:20 are, generally, found to be the most effective.

In general, the nature of the drying gas to be employed in the shock-drying process of the present invention, is not critical, provided it can be loaded with a sufficient amount of vaporized solvent in a sufficiently brief space of time and does not interfere with a chemical conversion if that has to take place in order to effect in situ formation of the desired catalytically active material. For economical reasons air is to be preferred, if it satisfies the conditions just set out. Examples of other drying gases which may often suitably be employed, include argon, helium, hydrogen, carbon dioxide, nitrogen and oxygen.

When oxygen or an oxygen-containing gas is employed in the shock-drying treatment of silver catalysts, this may result in the proportion of metallic silver being reduced and that of silver oxide being increased. This is by no means objectionable and it may even be desirable to effect a partial or even complete conversion of metallic silver into silver oxide by a heat treatment with oxygen or air following the shock-drying treatment which has been carried out with the use of non-oxidizing drying-gas. Suitable temperatures of the particles during the shock-drying treatment are, generally, above 250°C, and preferably between 300 and 550°C. Of course, the temperatures of the gaseous heating media will as a rule be higher, for example, 700 or even 1000°C.

When the shock-drying treatment is carried out by letting the particles to be dried fall through a heated and fluidized bed of an inert particulate solid substance, the fluidized state of the particles of this inert substance is, of course, maintained by means of the upward stream of the drying gas. The temperature of the fluidized bed can be regulated according to circumstances, such as the material to be dried, the type of solvents to be removed and the type of chemical conversions take place during the drying treatment. However, when shock-drying silver catalysts, temperatures ranging from 200° to 900°C are as a rule the most suitable temperatures varying from 400°

70

75

80

85

90

95

100

105

110

115

120

125

130

to 800°C being usually found to be preferable. In general, the temperatures required are lower than those discussed above for the case when only a stream of drying gas is employed without a bed of fluidized particles.

When in the production of silver catalysts the chemical conversion of the original silver compounds into metallic silver and/or silver oxide is effected simultaneously with the shock-drying treatment, this leads to superior properties of the resulting silver catalysts for use in the oxidation of olefins to olefin oxides as compared with catalysts comprising the same proportions of the same ingredients but prepared by some other method.

When using silver catalysts prepared in accordance with the present invention in the direct oxidation of an olefin with molecular oxygen to the corresponding olefin oxide, conventional conditions, as known in the art, may generally be applied. Such conditions relate, for instance, to temperatures, pressures, residence times, presence or absence of diluent materials, including, for instance, nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, and presence or absence of moderating agents to control the catalytic action, for example, 1,2-dichloromethane or chlorinated polyphenyl compounds. Further conditions relate, for instance, to recycling of materials to a reaction zone or the use of a series of reaction zones in order to increase the yields of the desired product, and the use of the catalysts in a fixed bed, or alternatively, in a fluidized bed.

#### EXAMPLE I

##### *Preparation of silver catalysts*

Two experiments, to be denoted by the numbers 1 and 2, were carried out using the shock-drying treatment of the invention and for comparison two other experiments, to be denoted by the numbers 3 and 4 were carried out without making use of a shock-drying treatment. In all these experiments the support material was a particulate alpha-alumina with a surface area of approximately 0.05 m<sup>2</sup>/g, a pore volume of 0.23 ml/g and a particle size between 0.074 and 0.300 mm. This support was previously dried by calcination in an oven at a temperature of 500°C for 2 hours; the dried support contained less than 0.1% w of water.

(1) The support material was impregnated with a solution of silver nitrate in a mixture of water and ethylene glycol containing 50% vol of water, the amount of impregnation liquid used being such that the pores were just completely filled with liquid. Thereafter the wet support was heated over a steam bath at 100°C with stirring until the particulate support acquired the nature of a free-flowing powder. At this stage the support contained 16.8% wt of liquid absorbed within the pores.

The support particles were then subjected to a shock-drying treatment by letting these particles fall in a vertically positioned glass tube at a rate of 25 g/h. An upward stream of oxygen having a temperature of 500°C, was passed through the tube at a rate of 5 l/h. The tube had a length of 40 cm and an internal diameter of 1 cm, the average residence time of the support particles in the tube was about 3.5 s. On leaving the tube, the support contained less than 0.1% wt of liquid constituents (determined at room temperature), thus indicating that the present rapid drying treatment had led to efficacious removal of absorbed liquid.

- (2) Experiment 1 was repeated with identical conditions, apart from the drying gas in the shock-drying treatment being air instead of oxygen. For the particles thus obtained the same content of liquid was found as in Experiment 1.
- (3) The support was impregnated with a solution of silver nitrate in water and subsequently pre-dried on a steam bath as described in experiment 1. Thereafter, the support was heated in an oven to 300°C in one hour and kept at that temperature for 2 hours. After cooling to room temperature the catalyst was ready and contained less than 0.1% wt. of liquid.
- (4) The support was impregnated with a solution of silver nitrate in water and subsequently pre-dried on a steam bath as described in experiment 1. Thereafter the impregnated support was completely dried, while the silver compound precipitated in the pores of the support was simultaneously reduced to metallic silver, by passing a mixture of 10% vol of hydrogen and 90% vol of nitrogen over the support at a temperature of 280°C during 2½ hours.

After cooling the catalyst was ready; its liquid content was below 0.1% w.

In experiments 1—4, in each particular case the amounts of silver compounds added to the support were so adjusted as to give all catalysts the same silver content of 10.8% w, calculated as metal on the weight of the support.

##### *Activity of catalysts*

The catalysts prepared in experiments 1—4 were tested in the oxidation of ethylene into ethylene oxide by means of molecular oxygen using a fluidized bed technique. In each test run 30 g of catalyst was mixed with 30 g of non-treated support particles and introduced into a glass tubular reactor with a length of 50 cm and an internal diameter of 2.5 cm. At a pressure of 1.08 atm. abs a gaseous mixture of ethylene and air, in a molar ratio of 1:19 was passed upwards through the catalyst bed with a space velocity (GHSV) of 1866 l/kg cat./h. The temperature of the fluidized bed

was now raised to 400°C and maintained at this level during 1 hour. Thereafter the temperature was lowered to 260°C and at this temperature the activity and selectivity of the catalysts were determined and expressed in terms of ethylene conversion and ethylene oxide selectivity. This conversion is calculated as a percentage from the equation  $C=100(1-X)$ , wherein X is the ratio of the molar amount of ethylene in the product gas and the molar amount of ethylene in the feed gas. Selectivity is calculated as a percentage from

the equation  $S = 100.Y$ , wherein Y is the molar ratio of the amount of ethylene oxide formed and the amount ethylene converted. It should be noted here that the experimental results given in Table I and in the other tables of the subsequent examples have each been determined independently per pass, in the test runs no recirculation of non-converted ethylene to the reactor being applied. Table I gives the figures found for the catalysts prepared in experiments 1—4.

TABLE I

Exp.	Preparation of Catalysts	Performance	
	Method applied	conversion, %	selectivity, %
1	shock-dried in O <sub>2</sub>	42.5	45.3
2	shock-dried in air	40.9	39.8
3	slowly dried at 300°C	23.5	38.5
4	reduced with H <sub>2</sub>	26.4	39.6

These results demonstrate the superiority of the catalysts of this invention (exp. 1 and 2) in combining a high activity with a high selectivity as compared with those prepared by other methods (exp. 3 and 4) not included within the scope of this invention.

## EXAMPLE II

*Effect of silver content of the catalysts.*  
Catalysts were prepared as described in

Example I, experiment 1. In the impregnation solutions used, the amount of silver nitrate was varied to give silver contents in the final catalysts of 10.8, 16.2 and 21.6, respectively (calculated as metal on support); the temperature of the drying gas was 540°C. All other conditions remained unchanged. The catalysts were tested as described in Example I.

TABLE II

Ag content of catalysts, % w	Performance	
	conversion, %	selectivity, %
10.8	42.3	45.2
16.2	46.8	46.4
21.6	52.5	47.4

## EXAMPLE III

*Effect of promoting compounds.*

A catalyst containing 21.6%w of silver was prepared as described in Example II. The activity of this catalyst was compared with those of other catalysts in which promoting lithium compounds had been incorporated.

The latter catalysts were prepared as follows:  
Before the support was impregnated with

the solution of silver nitrate in a water/ethylene glycol mixture containing 50%v of water, the support was impregnated with an aqueous solution of lithium hydroxide and subsequently dried at a temperature of 200°C for 2 hours. The procedure given in Example II was followed.

To prepare another catalyst, this experiment was repeated using lithium nitrate instead of

lithium hydroxide, all other conditions remaining unchanged.

5 A third catalyst was prepared employing simultaneous addition of lithium and silver compounds by impregnating the support with a solution of silver nitrate and lithium nitrate in a mixture of water and ethylene glycol containing 50%v of water and thereafter following the procedure of Example II.

10 A fourth catalyst was prepared by starting with the 21.6%w silver catalyst described in Example II, impregnating this catalyst with a

solution of lithium hydroxide in water and drying the impregnated catalyst thus obtained by heating in air at a temperature of 200°C for 2 hours. 15

The amounts of lithium compounds and silver compounds used to prepare these promoted catalysts were such that each catalyst contained 0.14%w of lithium (calculated as metal on support) and 21.6%w of silver (calculated as metal on support). 20

All catalysts were subjected to the testing method described in Example I.

TABLE III

Preparation of Catalysts, order of addition		Performance	
1	2	conversion, %	selectivity, %
Ag	none	52.5	47.4
Li	Ag	44.5	59.6
Li*	Ag	40.1	58.0
Ag + Li*	none	35.5	53.8
Ag	Li	33.3	41.7

\* added as nitrate.

The results of this table illustrate the preference for adding the promoting compounds prior to the addition of the silver compounds to the support.

#### EXAMPLE IV

##### *Heat-treatment of promoters*

30 Catalysts were prepared by addition of lithium hydroxide prior to the impregnation with silver nitrate solution as described in Example III. The procedure followed here 35 differed from that given in the said Example in that different amounts of silver nitrate were used. The final catalyst now contained 0.14%w lithium and 10.8%w silver (calculated as metals on the weight of the support). 40

Furthermore, between the impregnation with lithium hydroxide and the addition of silver nitrate, the supports were heated in air at temperatures between 400 and 900°C for periods of 2 hours in each particular case. The remaining conditions were all identical with those given in the relevant experiment of Example III. 45

To test the performance of the catalysts thus obtained, 40 g of catalyst was mixed with 40 g of non-treated support and introduced into the reactor described in Example I. Apart from the space velocity, now being 1400 l/kg cat/h, all other conditions were identical with those given for the test runs of Example I. 50 55

TABLE IV

Preparation of catalysts, promoter activated at	Performance	
	conversion, %	selectivity, %
400°C	49.3	70.2
500°C	46.1	75.2
550°C	48.2	61.8
600°C	54.5	59.3
900°C	60.4	40.7

## EXAMPLE V

*Fixed-bed experiments*

For the purposes of comparison a number of different catalysts were prepared starting from an alpha-alumina support having a surface area of less than 1 m<sup>2</sup>/g, a pore volume of 0.2 ml/g and a particle size between 0.6 and 1.6 mm. This support contained less than 0.1%w of water.

The first catalyst (A) was prepared by impregnating the support with an aqueous solution of lithium hydroxide, drying and heating the impregnated support in air at a temperature of 450°C for 2 hours and subsequently impregnating the support with a solution of silver nitrate in a ethylene glycol/water mixture containing 75%v of water. The impregnated support was predried over a steam bath to a liquid content of 7.8%w and then shock-dried, applying air with a temperature of 900°C as the drying atmosphere, the other conditions of the shock-drying treatment being identical with those described in Experiment I, Example I. After the shock-drying the catalyst was ready; it contained 0.14%w of lithium, 10.8%w of silver (calculated as metals on support) and less than 0.1%w of liquid constituents.

To prepare catalyst B, this experiment was repeated at identical conditions, apart from the shock-drying atmosphere now being nitrogen. Before being tested this catalyst was heated in air at 500°C for 6 hours. The composition of the final catalyst was 10.8%w of silver and 0.14% of lithium, calculated as metals on support.

Catalyst C was obtained by repeating the procedure given for catalyst A but omitting the addition of lithium hydroxide.

Catalyst D was produced by impregnating the support with an aqueous solution of silver nitrate and predrying the wet support over a steam bath. Thereafter, the procedure given in Experiment 4 of Example I was repeated. Catalysts C and D each contained 10.8%w of

silver, calculated as metal on support.

The activities and selectivities of these catalysts were now determined by comparatively oxidizing ethylene to ethylene oxide in a fixed catalyst bed at a pressure of 1.08 atm. abs, a contact time of 8.4 seconds, and temperatures between 230 and 288°C in a reactor consisting of a glass tube having an internal diameter of 15 mm and an length of 85 cm. This reactor was immersed in an externally heated fluidized bed of powdered silica-alumina particles acting as heat transfer medium. In each run 100 g of catalyst were placed in the reactor giving a catalyst bed length of 60 cm. The gaseous mixtures brought into contact with the catalysts comprised 25%v ethylene, 8.7%v oxygen and 66.3%v nitrogen, or 3%v ethylene and 97%v air, respectively. Each of these mixtures contained  $3 \times 10^{-4}$ %m, based on the molar amount of ethylene, of the chlorinated polyphenyl compound "Aroclor" 4465 as moderator (Aroclor is a Registered Trade Mark).

In each run an initial period of 400 hours' operation at a constant temperature of 280°C and space velocity of 340 l/kg cat./h preceded the actual test run, which was effected at the conditions given hereinbefore. In these runs the temperatures were varied in order to find comparative conversion percentages; the experiments were carried out without applying recirculation of non-converted ethylene to the reactor.

The performance of catalysts A—D are reported in Table V. It is clearly apparent that the conversion/selectivity levels of the catalysts of this invention (A—C) are better than that of the comparative catalyst (D). It is added here that the catalyst A showed a constant performance during more than 3800 hours, thus indicating the excellent stability of this catalyst. The runs with catalysts B and C were continued for more than 580 hours and more than 1200 hours, respectively. In



these prolonged runs, too, no decrease in catalytic activity and selectivity could be observed.

TABLE V

Conditions					Performance				
Feed, molar ratio $C_2H_4 : O_2 : N_2$	Temp. °C.		C	D+	conversion, %m	selectivity, % m			
cat. A	B					cat. A	B	C	D+
25.0 : 8.7 : 66.3	262	247	255	236	9.6	78.7	79.3	75.9	69.2
25.0 : 8.7 : 66.3	270	253	262	255	12.3	76.9	77.5	74.2	68.3
25.0 : 8.7 : 66.3	280	264	272	278	16.4	75.2	75.4	71.0	65.8
25.0 : 8.7 : 66.3	287	276	—	—	19.8	73.7	72.9	—	—
$C_2H_4$ : air									
3 : 97	249		256	258	43.8	82.9		76.7	70.4
3 : 97	260		256	276	60.6	80.3		72.7	68.2
3 : 97	—		—	288	67.0	—		—	66.5
3 : 97	278		279	—	88.3	73.5		67.2	—

+ for comparison, not according to this invention.

## EXAMPLE VI

## Oxidation of propylene.

5 Catalyst A described in Example V was tested in the oxidation of propylene to propylene oxide at temperatures of 240°C and 328°C, respectively, a pressure of 1.08 atm. abs., a contact time of 9 seconds and a space velocity (GHSV) of 300 1/kg cat./h. The gaseous mixture which was contacted with the catalyst comprised 25 %m of propylene, 10 %m of oxygen and 65 %m of nitrogen. No preceding reaction period being applied, the remaining conditions were the same as described in Example V.

10 The conversion of propylene was 2 %m and the selectivity to propylene oxide was 55 %m at 240°C. At 328°C the conversion was 5 %m and the selectivity towards propylene oxide was 20 %m.

## EXAMPLE VII

25 150 g of a commercial alpha-alumina with a pore volume of 0.17 cm<sup>3</sup>/g and a surface area of approximately 0.05 m<sup>2</sup>/g, in the form of pellets with a diameter of 5 mm, was impregnated with an aqueous solution of 0.62 g lithium hydroxide in 25.5 ml water. The pellets were calcined at 450°C for two hours; they contained 0.26% w Li<sub>2</sub>O. The pellets so obtained were impregnated with a solution of 25.5 g silver nitrate in a mixture of 19.1 g water and 7.1 g ethylene glycol.

35 In a vertically placed cylindrical reactor

with a diameter of 4 cm and a length of 72.5 cm, 500 g of a powdered commercial alpha-alumina with a maximum particle diameter between 0.053 and 0.297 mm, a pore volume of 0.18 cm<sup>3</sup>/g and a surface area of less than 1 m<sup>2</sup>/g was fluidized by means of a stream of air. The reactor was kept at a temperature of 600°C. The height of the column of fluidized particles in the reactor was about 50 cm.

45 The impregnated pellets were dried by dropping them through the fluidized bed at a rate of about 1500 g/h. The residence time of each pellet in the fluidized bed was between 5 and 15 seconds.

50 The dried pellets were collected at the bottom of the cylindrical reactor. The solvents had been thoroughly removed, since heating of the dried pellets at 500°C for six hours resulted in a weight loss of only 0.6 g.

55 The pellets so obtained showed good catalytic activity in the oxidation of ethylene to ethylene oxide with the aid of oxygen, which is illustrated by the following experiment. 100 g of the pellets were broken to particles with a diameter of 0.6—1.2 mm, and of these particles a fixed bed was prepared. Over this bed a stream consisting of 25% methylene, 8.7% m oxygen and 66.3% m nitrogen (and containing 0.38 ppm of a chlorinated polyphenyl) was led at a velocity of 104 l gas per kg catalyst per hour, a temperature of 275—278°C and a residence time of 9.7 seconds.

40

45

50

55

60

65

The ethylene conversion was 5%, the selectivity to ethylene oxide was 66.1% of the ethene converted, the remainder of the ethene converted being oxidized to carbon dioxide.

#### 5 EXAMPLE VIII

150 g pellets, with a diameter of 5 mm, of the commercial  $\alpha$ -alumina described in Example I were impregnated with a solution of 25.5 g silver nitrate in a mixture of 19.1 g

10 water and 7.1 g ethylene glycol.  
In a vertically placed cylindrical reactor with a diameter of 10 cm and a length of 75 cm, 2000 g of a powdered commercial  $\alpha$ -alumina with a maximum particle diameter between 0.053 and 0.297 mm, a pore volume of 0.18 cm<sup>3</sup>/g and a surface area of less than 1 m<sup>2</sup>/g, was fluidized by means of a stream of air. The reactor was kept at a temperature of 500°C. The height of the column of fluidized particles was about 40 cm.

The impregnated pellets were dried by dropping them through the fluidized bed at a rate of 1500 g per hour. The residence time of each pellet in the fluidized bed was between 8 and 15 seconds.

The dried pellets were collected at the bottom of the cylindrical reactor. The solvents had been thoroughly removed, since heating of the dried pellets at 500°C for six hours resulted in a weight loss of only 0.5 g.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of a silver containing catalyst, which comprises impregnating a particulate solid porous substance with a solution of a reducible silver compound and subsequent evaporation of the solvent by intimately contacting the particulate porous solid substance with a heated gaseous atmosphere under such conditions that at least 80% by volume of the liquid adsorbed by the solid porous substance is evaporated in at most 900 seconds and reduction occurs simultaneously.

2. A process as claimed in claim 1, in which at least 90% by volume of the liquid is evaporated in at most 300 seconds.

3. A process as claimed in claim 2, in which substantially complete evaporation is effected in a time between 0.5 and 120 seconds.

4. A process as claimed in claim any one of claims 1 to 3, in which the impregnated porous substance to be dried consists of particles having a maximum particle diameter, as hereinbefore defined, of 1—25 mm, and in which the drying is effected by intimately contacting this particulate solid substance with a heated gaseous atmosphere, which comprises an added amount of inert solid material, the heated gas maintaining the said inert solid material in a fluidized condition, the fluidized inert solid material consisting of particles having a maximum diameter, as hereinbefore defined, of 0.5 mm and the particles to be dried

being transported by gravity through the fluid bed.

5. A process as claimed in claim 4, in which the inert solid material having a maximum particle diameter of 0.5 mm is a substantially non-porous substance or a porous substance having a surface area of less than 1 m<sup>2</sup>/g.

6. A process as claimed in claim 4 or 5 in which the inert solid material having a maximum particle diameter of 0.5 mm has a maximum particle diameter between 0.035 and 0.35 mm.

7. A process as claimed in any one of claims 4—6, in which the temperature of the fluidized bed is from 200 to 900°C.

8. A process as claimed in claim 7, in which the temperature of the fluidized bed is from 400 to 800°C.

9. A process as claimed in any one of claims 4—8, in which the solid substances to be dried have a maximum particle diameter of 2—9 mm.

10. A process as claimed in claim 9, in which the solid substances to be dried have a maximum diameter of 3—7 mm.

11. A process as claimed in any one of claims 1—10, in which the gaseous atmosphere is air.

12. A process as claimed in any one of claims 1 to 11 in which the impregnating solution contains a reducing agent.

13. A process as claimed in claim 12, in which the reducing agent is an organic reducing agent.

14. A process as claimed in claim 12 or 13, in which the solid porous substance has been impregnated with a solution of a silver compound in a mixture of a reducing agent and water as the solvent, the ratio by weight of the reducing agent and water in the solvent preferably being in the range of from 80:20 to 20:80.

15. A process as claimed in any one of claims 12—14, in which the reducing agent is a polyhydric alcohol.

16. A process as claimed in claim 15, in which the reducing agent is ethylene glycol.

17. A process as claimed in any one of the preceding claims, in which the silver compound is silver nitrate.

18. A process as claimed in any one of the preceding claims, in which the amount of silver introduced into the solid porous substance is such as to provide for a silver content between 5 and 15 %w, calculated as silver metal on the weight of the solid porous substance in the catalyst after the drying.

19. A process as claimed in any one of the preceding claims, in which the particulate solid porous substance is an aluminium oxide.

20. A process as claimed in claim 19, in which the solid porous substance is alpha-alumina.

21. A process as claimed in any one of the preceding claims, in which silver catalysts

are prepared which comprise one or more compounds of alkali or alkaline earth metals as promoters.

5 22. A process as claimed in claim 21, in which the catalyst comprises a lithium compound as the promoter.

10 23. A process as claimed in claim 21 or 23, in which the promoter is added to the particulate solid porous substance before it is impregnated with the silver-containing solution.

15 24. A process as claimed in claim 23, in which the addition of the promoter is effected by impregnating the particulate solid porous substance with an aqueous solution of one or more alkali metal and/or alkaline earth metal compounds and heat-treating the impregnated substance to effect conversion of the metal compounds into their oxides.

20 25. A process as claimed in claim 24, in which the heat treatment is effected at a temperature between 400 and 550°C.

25 26. A process as claimed in any one of claims 21—25, in which the amount of the promoter in the catalyst is between 0.03 and 0.5%w, calculated as metal on the weight of the solid porous substance.

27. A process as claimed in claim 1 and

substantially as hereinbefore described, with special reference to the Examples, excluding comparative matter contained therein. 30

28. Catalyst compositions, whenever prepared by means of a process as claimed in any one of the preceding claims.

29. A process for the preparation of olefin oxides by oxidation of olefins, in which a silver catalyst is employed as claimed in claim 28. 35

30. A process as claimed in claim 29, in which the olefin is ethylene.

31. A process as claimed in claim 29, in which the olefin is propylene. 40

32. A process as claimed in any one of claims 29—31 and substantially as hereinbefore described with particular reference to the Examples, excluding comparative matter contained therein. 45

33. Olefin oxides whenever prepared by a process as claimed in any one of claims 29—32.

WILLENS AND ROBBINS,  
Chartered Patent Agents,  
Shell Centre,  
London, S.E.1.  
Agents for the Applicants.

**THIS PAGE BLANK (USPTO)**

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**